METHOD OF DEINKING

The present invention relates to a method of deinking printed wastepaper.

Growing awareness of environmental damage caused by deforestation has seen an increase in the recycling of wastepaper in recent years. It has been recognised that the ability to recycle wastepaper is commercially advantageous and has a significant impact on the conservation of virgin fibre resources. However, technological advances in printing inks and print media present ever-growing challenges to recyclers.

Printing on paper is typically accomplished using one of two types of ink, namely, impact ink, which is physically pressed onto the paper, and non-impact ink, which is attracted to a charged image and is then transferred to the paper. Impact inks are typically wet inks, for example letterpress inks, offset litho inks, photogravure inks and flexographic inks. For example, letterpress inks are generally composed of carbon black pigment in a mineral oil vehicle and are used in, for example, newspaper printing. Offset litho inks tend to contain more pigment than letterpress inks and contain drying oils such as linseed or alkyl resins. Flexographic inks are used in similar processes to letterpress inks but are water-based and contain emulsified ink in an alkali soluble binder. Such inks may easily be dislodged, but may form extremely fine particles that are difficult to capture and remove.

Non-impact inks, e.g. toners, are generally dry, powdered inks and are used in laser printing, photocopying and facsimile machines and generally comprise thermoplastic resins and pigment.

The deinking of paper bearing these two different types of ink requires different deinking procedures and conditions.

Conventionally, deinking of paper bearing non-impact ink merely requires pulping with a surfactant in neutral conditions, whereas paper bearing impact ink requires different conditions, such as treatment with alkali, silicate and peroxide, as well as a surfactant.

In conventional deinking methods, the wastepaper is disintegrated (pulped) by mechanical agitation in an aqueous medium to separate the ink and impurities from the paper fibre and disintegrate the ink into particles of approximately 0.1 to 1000 µm. A grey slurry is thus obtained in which the ink is present in a finely dispersed form. The impurities, for example, plastic, aluminium foil, stones, screws, staples, paper clips etc., are removed during a large number of screening steps.

Whilst ink detachment of non-impact, e.g. photocopy, paper can normally be achieved in neutral conditions, for other printed paper ink detachment is routinely accomplished at alkaline pH levels using alkali hydroxides, alkali silicates, oxidative-working bleaches and surfactants at temperatures between 30 and 50°C. Usually, anionic and nonionic tensides are used as surfactants, for example, soaps, ethoxylated fatty alcohols and/or ethoxylated alkyl phenols (see, for example, EP 0013758).

The ink particles are then removed from the fibre slurry by washing and/or flotation. Smaller ink particles are removed by washing, and larger ink particles and stickies (i.e. glue residues and adhesives) are removed by flotation. During flotation, air bubbles are blown into the pulp. The dispersed ink particles become attached to the air bubbles, which carry the ink particles to the surface. The resultant foam is then skimmed from the surface. Subsequent steps involve heating the pulp to evenly distribute stubborn ink particles and screening the pulp to separate the damaged,

short or weak fibres. The remaining clean pulp is then pressed between rollers into sheets and dried.

Thus, efficient deinking demands both successful separation of the ink from the paper fibre and removal of the dispersed ink from the fibre slurry.

However, there are a number of disadvantages associated with traditional deinking methods. For example, the incomplete removal of ink particles from the fibre slurry can cause the resulting paper to have a grey hue, spotting, and a low degree of brightness. Brightness and colour are important quality criteria for many paper uses.

In addition, the alkaline conditions used in traditional deinking methods cause water-soluble and/or colloidal solids and finely dispersed solids to contaminate the process water, for example, fillers, fine fibres and stickies. If these contaminants are insufficiently removed during washing, they can be concentrated by subsequent washings and reintroduced to the paper fibre, causing a loss of brightness in the resultant paper. Effluent containing the aforementioned chemicals conventionally used in deinking methods is also environmentally undesirable.

The present invention seeks to provide a method of deinking wastepaper which can overcome disadvantages of conventional deinking methods.

According to the present invention there is provided a method of deinking printed paper, the method comprising pulping the paper to form an aqueous slurry, adding a deinking additive to the paper, and removing detached ink by flotation, wherein the additive comprises an organo-modified siloxane comprising units of the formula:

$$[R^1_aZ_bSiO_{(4-a-b)/2}]_n$$

in which each R^1 is independently selected from a hydrogen atom, an alkyl, aryl, alkenyl, aralkyl, alkaryl, alkoxy, alkanoyloxy, hydroxyl, ester or ether group;

each Z is independently selected from an alkyl group substituted with an amine, amide, carboxyl, ester, or epoxy group, or a group $-R^2-(OC_pH_{2p})_q(OC_rH_{2r})_s-R^3$;

n is an integer greater than 1;

a and b are independently 0, 1, 2 or 3;

R^2 is an alkylene group or a direct bond;

R^3 is a group as defined for R^1 or Z above;

p and r are independently an integer from 1 to 6;

q and s are independently 0 or an integer such that $1 \leq q + s \geq 400$;

and wherein each molecule of the organo-modified siloxane contains at least one group Z.

Z is preferably a group $-R^2-(OC_pH_{2p})_q(OC_rH_{2r})_s-R^3$, more preferably wherein p and/or r are independently 2, 3 or 4, i.e. a group comprising ethylene, propylene, and/or butylene oxide groups. Preferably, q and s are each independently integers from 10 to 30, more preferably 15 to 25 (for example 18). In a particularly preferred group Z, p is 2, r is 3, and q and s are both 18. R^2 may be an alkylene group, for example having from 1 to 6 carbon atoms (i.e. a methylene, ethylene, propylene, butylene, pentylene or hexylene group), or a direct bond. R^3 may be a group as defined hereinabove for R^1 or Z, and is preferably a hydrogen atom or a hydroxyl group.

Additionally or alternatively, Z may be an alkyl group substituted with an amine, amide, carboxyl, ester, or epoxy group, for example an alkyl group having from 1 to 6 carbon atoms, i.e. a substituted methyl, ethyl, propyl, butyl, pentyl or hexyl group.

The siloxane may be linear or may comprise units in which $a + b = 0$ or 1, i.e. the siloxane may contain branching. When

Z is a group $-R^2-(OC_pH_{2p})_q(OC_rH_{2r})_s-R^3$, R^3 is preferably a hydroxyl or alkanoyloxy group.

Preferably, 2 to 20 mole percent of silicon atoms in the siloxane molecule are substituted by a group Z, more preferably 5 to 16 mole percent.

The siloxane preferably has a hydrophilic/lipophilic balance (HLB) in the range of 5.0 to 7.3.

The molecular weight of the siloxane is preferably in the range of 1,000 to 500,000, more preferably 10,000 to 100,000.

A particularly preferred siloxane for use in the present invention is a hydroxy-endcapped linear polydimethylsiloxane having an HLB of 5.9 to 6.3, in which 10 to 12 mole percent of silicon atoms are substituted by Z groups of the formula $-R^2-(OC_pH_{2p})_q(OC_rH_{2r})_s-R^3$, in which p is 2, r is 3 and q and s are both 18, R^2 is an alkylene group having from 1 to 6 carbon atoms or a direct bond, and R^3 is a hydrogen atom or a hydroxyl, ester or ether group.

The additive used in the present invention may comprise further components, in addition to the organo-modified siloxane. For example, the additive may further comprise one or more components selected from a polydimethylsiloxane, an organic polyether, and a fatty acid. Suitable organic polyethers include those of the formula $R^4-(OC_pH_{2p})_q(OC_rH_{2r})_s-R^5$ in which R^4 and R^5 are selected from a hydrogen atom, hydroxyl, alkyl and alkoxy groups, and p, q, r and s are as defined hereinabove. Suitable fatty acids include saturated and unsaturated monobasic aliphatic carboxylic acids, for example having from 8 to 22 carbon atoms, such as lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, palmitolic, oleic, linoleic, linolenic, and arachidonic acids.

The additive may be in the form of an emulsion, for example the organo-modified siloxane may be a gum based self-emulsifying siloxane.

In the method of the present invention, the additive may be added to the paper before, during or after pulping. The amount of additive to be added to the paper is preferably within the range 0.1 to 1 wt% of the paper, more preferably 0.1 to 0.5 wt%. The additive may, for example, be added to the paper neat, as an emulsion, or in solution, for example an aqueous solution.

The method of the present invention is preferably performed at substantially neutral pH, although the method may be performed under alkaline pH.

The pulping and ink removal steps of the present invention may be performed as is conventional, as will be familiar to a person skilled in the art and described hereinabove. For example, the paper may be pulped to form an aqueous slurry having a consistency of, for example, from 1 to 10% (for example, 1 to 5%) at a temperature of between 30 and 50°C, for example 35 to 45°C. Consistency is defined as wt% of pulp solids in the fibre suspension. Ink removal may be performed in a suitable flotation cell (for example, a Denver Lab flotation cell) at a suitable temperature, for example between 30 and 50°C (e.g. 35 to 45°C), and number of revolutions per minute, for example from 500 to 1000 rpm. An additional advantage associated with the method of the present invention is that when used to treat flexographic printed waste, the process water is relatively clear, whereas with known deinking methods it is generally black. Moveover, the present method produces pulp of improved brightness.

Embodiments of the present invention will now be described in detail.

Example 1

a) Pulping

To an aqueous suspension of 110g of air-dry wastepaper

(50% newspaper and 50% magazine paper) having a consistency of 4% were added 440g of industrial water at 45°C in a mixing vessel. The suspended paper was kneaded for 15 minutes at 45°C.

b) Ink removal

Water having a hardness of 16°dH was added to the pulp obtained in a) above to achieve a consistency of 1%. To the pulp varying amounts of a hydroxyl endcapped polydimethylsiloxane having approximately 11 mole % silicon atom substitution by $-(OC_2H_4)_{18}(OC_3H_6)_{18}$ side chains, an HLB of approximately 6.1 and a molecular weight of approximately 60,000 (referred to herein as Siloxane 1) was added as an aqueous solution. The pulp was floated for 8 minutes at 45°C in a Denver Lab Flotation Cell at 1000 rpm, after which the pulp was separated from the water, and formed into sheets between two filters of a sheet former with drying at 95°C for 10 minutes under vacuum.

By way of comparison, steps a) and b) above were repeated using a commercially available fatty acid based deinking preparation. The results are shown in Table 1 below. Whiteness was evaluated according to DIN 53145 Part 1.

Table 1

Additive	wt % of additive used	Paper	pH	Whiteness before flotation %	Whiteness after flotation %	Whiteness difference %
Fatty acid	0.4	aged	8.5	42.4	59.0	16.6
Fatty acid	0.4	fresh	7.2	43.6	51.3	7.7
Siloxane 1	0.3	aged	8.5	46.6	61.9	15.3
Siloxane 1	0.3	fresh	8.5	46.6	61.9	15.3
Siloxane 1	0.3	fresh	7.2	46.5	59.1	12.6
Siloxane 1	0.1	fresh	7.2	44.6	56.5	11.9
Siloxane 1	0.3	aged	7.2	40.2	47.8	7.6

Example 2

a) Pulping

To an aqueous suspension of 110g of air-dry wastepaper (10% newspaper and 90% magazine paper) having a consistency of 20% were added 440ml of industrial water at 45°C in a mixing vessel. The suspended paper was kneaded for 15 minutes at 45°C.

b) Ink removal

Water was added to the pulp obtained in a) above to achieve a consistency of 1.09%. To the pulp varying amounts of a hydroxyl endcapped siloxane as defined in Table 4 below were added as an aqueous solution. The pulp was floated for 8 minutes at 45°C in a Denver Lab Flotation Cell.

Steps a) and b) above were repeated using the siloxane used in Example 1 (Siloxane 1) and the siloxanes defined in Table 4 (Siloxanes 2 to 8) on fresh and aged wastepaper. Table 4 also contains viscosity data for each of the siloxanes. By way of comparison, the experiment was also carried out using the commercially available fatty acid based deinking preparation used in Example 1. The results are shown in Table 2 (fresh wastepaper) and Table 3 (aged wastepaper) below. Whiteness was evaluated according to DIN 53145 Part 1.

Table 2

Additive	wt % of additive used	pH	Whiteness before flotation %	Whiteness after flotation %	Whiteness difference %
Fatty acid	0.4	8.1	35.8	51.1	15.3
Siloxane 1	0.3	7.5	39.4	56.5	17.1
Siloxane 2	0.3	7.5	39.1	54.2	15.1
Siloxane 3	0.3	7.5	40.2	55.0	14.8
Siloxane 4	0.3	7.5	37.8	55.0	17.2
Siloxane 5	0.3	7.5	39.0	52.6	13.6
Siloxane 6	0.3	7.5	41.2	53.5	12.3
Siloxane 7	0.3	7.5	39.5	57.1	17.6
Siloxane 8	0.3	7.5	40.1	54.0	13.9

Table 3

Additive	wt % of additive used	pH	Whiteness before flotation %	Whiteness after flotation %	Whiteness difference %
Fatty acid	0.4	7.8	36.3	44.6	8.3
Siloxane 1	0.3	7.3	37.0	47.8	10.8
Siloxane 4	0.3	7.3	37.0	50.3	13.3
Siloxane 7	0.3	7.3	37.5	48.0	10.5

Table 4

n (degree of polymerisation)	% Substituted Silicon atoms		
	5	10	15
100	Siloxane 2 7,720 cP	Siloxane 3 5,560 cP	Siloxane 4 3,100 cP
300	Siloxane 5 98,540 cSt	Siloxane 6 6,060 cP	Siloxane 7 5,090 cP
500			Siloxane 8 6,830 cP

Example 3

a) Pulping

To an aqueous suspension of 110g of air-dry wastepaper (100% newspaper) having a consistency of 20% were added 400ml of industrial water at 45°C in a mixing vessel. The suspended paper was kneaded for 15 minutes at 45°C.

b) Ink removal

Water was added to the pulp obtained in a) above to achieve a consistency of 1.09%. To the pulp varying amounts of a hydroxyl endcapped siloxane as defined in Table 4 and Example 1 were added as an aqueous solution. The pulp was floated for 8 minutes at 45°C in a Denver Lab Flotation Cell.

Steps a) and b) above were repeated using the siloxane used in Example 1 (Siloxane 1) and two of the siloxanes defined in Table 4 (Siloxanes 4 and 7). By way of comparison, the experiment was also carried out using the commercially available fatty acid based deinking preparation used in Example 1. The results are shown in Table 5 below. Whiteness was evaluated according to DIN 53145 Part 1.

Example 4

Steps a) and b) of Example 1 were repeated using the siloxane used in Example 1 (Siloxane 1), but were performed on 100% flexographic paper. In addition, 0.10 wt% sodium hydroxide and 1.20 wt% sodium silicate were added to the slurry.

By way of comparison, the experiment was also carried out using the commercially available fatty acid based deinking preparation used in Example 1. The results are shown in Table 6 below. The appearance of the filtration water was also recorded. Whiteness was evaluated according to DIN 53145 Part 1.

Table 5

Additive	wt % of additive used	pH	Whiteness before flotation %	Whiteness after flotation %	Whiteness difference %
Fatty acid	0.4	7.7	24.7	27.0	2.3
Siloxane 1	0.3	7.3	26.5	33.0	6.5
Siloxane 4	0.3	7.2	24.4	33.0	8.6
Siloxane 7	0.3	7.3	26.0	35.0	9.0

Table 6

Additive	wt % of additive used	Whiteness before flotation %	Whiteness after flotation %	Whiteness difference %	Appearance of filtration water
Fatty acid	0.4	28.8	29.9	1.1	Dark black
Siloxane 1	0.2	25.4	33.4	8.0	Light grey
Siloxane 1	0.2	26.6	34.5	7.9	Light grey